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(54) Preparation of zeolite coated substrates.

(57) Zeolite-coated substrates, and particularly magnetizable particles suitable for use in a magnetically stabilized fluidized bed, are prepared by introducing the substrate, preferably magnetizable particles such as magnetite or iron, into a reaction mixture for forming a zeolite having adsorbent properties, such as zeolite Y, heating the reaction mixture and mixing so that there is relative movement of the substrate within the reaction mixture such that the zeolite is preferentially formed as a coating on the substrate.

EP 0 149 343 A1

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PREPARATION OF ZEOLITE COATED SUBSTRATES 0149343

1 This invention relates to the preparation of zeolite-
coated substrates which may be used as catalysts or
adsorbents, and particularly to the preparation of
magnetizable zeolite compositions useful in forming
5 fluidized beds of magnetically stabilized particles.

There are many applications where it is useful to have
a zeolite deposited on a substrate to improve surface
area to weight ratio of the zeolite or to provide
strength or a particular form.

10 GB 1 245 349 discloses extended zeolite structures in
which extended supports are coated first with a layer
of hydrated alumina which is then reacted to form a
zeolite thereon.

US 3 730 920 discloses a method for producing zeolite
15 surfaced substrates (particularly inorganic oxides such
as silicon oxides and aluminium oxides) by contacting
the substrate with aluminosilicate or with a zeolite
yielding mixture. Contact between the substrate and a
zeolite yielding mixture is effected by stirring.

20 EP 0 055 044 describes a catalyst composition comprising
a crystalline modified-silica zeolite overlying a silica
core with the same crystalline structure as the zeolite.
These compositions are prepared by introducing performed
particles of silica into a synthesis gel for the zeolite
25 so that the zeolite forms on the silica particles. GB
2 097 374 describes a particulate crystalline material

1 comprising a core of intermediate pore size crystalline
silicate within an outer shell with the same crystal
structure and comprising an aluminosilicate. There is
no indication within these documents of how a zeolite
5 layer may be formed on a substrate which does not have
the same crystal structure as the zeolite.

GB 1 567 948 describes the use of zeolite seeds in the
preparation of aluminosilicates of the ZSM-5 family in
which the a reaction mixture for forming the zeolite
10 and the seeds are heated to bring about the formation
of the ZSM-5 zeolite. The reaction mixture may be
stirred. EP 0 002 960 describes the seeding of a
reaction mixture for forming zeolite A with preformed
zeolite A. Seeding as such is a well-known technique
15 for initiating crystallization but is not regarded as a
means for forming a crystalline layer upon a substrate.
Indeed, GB 1 567 948 makes it clear that when the seeds
used in the described process do not have the ZSM-5
structure the product is a ZSM-5 zeolite and there is
20 no disclosure of any composite product.

GB 1 124 524 describes a granulation technique in which
preformed zeolite particles are formed into granulates
with inorganic binding agents, in which technique
zeolite particles and powdered binding agent are
25 agglomerated with water in a rotating vessel, preferably
with an oblique axis of rotation, to form granules,
which are built up layerwise to 0.2 to 10 mm in diameter.

1 This is a process for forming agglomerates of a large
number of zeolite and binder particles from preformed
zeolites and gives no direction to the formation of
zeolite layers on the surface of discrete substrate
5 bodies. EP 0 021 267 describes a similar granulation
technique for use in preparing detergent granules.

Zeolites are particularly useful in adsorption processes,
and it has now been found that a highly effective adsor-
bent particle for use in magnetically stabilized fluidi-
10 zed beds may be prepared by forming a zeolite around
a magnetizable core, preferably so that the zeolite
substantially covers the core, and that the resulting
particle has a number of advantages over conventional
magnetizable composites containing zeolites.

15 It is known that a fluidized bed of magnetizable
particulate solids can be subjected to a magnetic field
and stabilized, and that such a bed is useful in
processes requiring fluid-solid contact.

In magnetically stabilized bed processes, like conven-
20 tional fluidized processes, a fluid is injected upwardly
at velocities sufficient to overcome the free fall
velocities of the individual particles (due to gravity)
and cause bed expansion and fluidization of the particles
without sweeping significant amounts of the particles
25 from the bed. In conventional fluidized processes,
however, the injection of fluid at velocity sufficient

1 to produce expansion of the bed (i.e., transform the
fixed packed bed to a fluidized bed) is accompanied by
significant bubble formation whereas, in contrast, in a
fluidized bed subjected to the influence of a magnetic
5 field there is an interim, or quiescent state wherein
there is little, if any, motion exhibited by the
particles within the fluidized bed. Within the magneti-
cally stabilized bed the formation of bubbles (with
gas) or chaunds (with a liquid) is virtually eliminated
10 and backmixing is suppressed allowing staging to be
achieved. For this reason, magnetically stabilized bed
processes offer advantages over both fixed and conven-
tional fluidized bed operations. They are superior to
conventional fluidized bed operations in that they
15 provide better counter-current contacting, low fluid
and solids back mixing, and lower particle attrition.
They are superior to fixed bed operations in that they
provide lower pressure drop, better ability to transfer
solids, and virtually eliminate bed plugging problems.
20 A process disclosing a magnetically stabilized bed and
its mode of operation for conducting catalytic reactions,
and the capture of particulates to provide a filtering
action is disclosed in US 4 115 927.

In much of the early work on catalytic processes the
ferromagnetic component constituted essentially the whole
25 of the particles in the bed. Compositions were also
developed comprising ferromagnetic inclusions dispersed

1 within matrices constituted in part of non-ferromagnetic
materials and processes for the subsection of beds of such
particles to the influence of a magnetic field are known.

US Patent 4 247 987 discloses forming a composite of a
5 magnetizable component and adsorbent (e.g. zeolite) by
admixing them with a base for the adsorbent (e.g. silica
or alumina) to form a gel which is dried, calcined and
sized. US Patent 4 252 679 discloses contacting a magnetic
10 alloy of iron or cobalt with a phosphate ion containing
solution to form a film thereon, then admixing with an
inorganic oxide matrix, followed by contacting with a
noble metal. The composite can be formed by cogellation
of the magnetic alloy particles with an inorganic oxide
support material (e.g. zeolite) preferably by admixture
15 in a slurry with an inorganic oxide precursor which is
precipitated from solution with the magnetic alloy
particles. US Patent 4 255 289 discloses an inorganic
oxide particulate admixed with magnetic alloy particles
and an inorganic precursor which serves as a binder.
20 US Patent 4 289 655 discloses a magnetic iron precursor
(illmenite, FeTiO_3) incorporated within an inorganic
oxide and heated in a reducing atmosphere to form
reduced iron metal dispersed throughout the composite.

This invention concerns an improved process for forming
zeolite layers on substrates which is particularly
25 useful in forming zeolite coatings on magnetizable
particles.

1 In one aspect this invention provides a process for the
preparation of a zeolite layer upon a substrate which
does not have the same crystalline structure as the
zeolite, in which process the substrate is contacted
5 with a reaction mixture for forming a zeolite and the
reaction mixture is heated to bring about zeolite
formation, in which the substrate is tumbled within
the reaction mixture during heating so as to cause
zeolite formation preferentially as a layer on the
10 surface of the substrate.

The invention enables the zeolite to be formed as a
layer on the substrate in preference to it being
formed as pure zeolite particles within the body of
the reaction mixture. It is believed that the mixing
15 technique employed results in the preferential forma-
tion of nucleation centres upon the substrate surface
rather than within the reaction mixture. Moreover, the
product of the process of the invention comprises
discrete substrate bodies coated with zeolite rather
20 than agglomerates of separate zeolite particles with
substrate bodies.

An important feature of the invention comprises tumbling
the substrate within the reaction mixture during
heating - that is to say, causing the substrate to be
25 raised and then allowed to fall through the reaction
mixture under gravity. This tumbling action is prefer-

1 ably achieved by introducing the substrate and the
reaction mixture into a rotatable vessel having an axis
inclined to the vertical and rotating the vessel during
at least a part of the time that the reaction mixture
5 is heated so as to bring about formation of zeolite in
the substrate.

The particular zeolite chosen will depend upon the
adsorption or separation which it is to be carried out
using the magnetically stabilized fluidized bed. For
10 example, when it is desired to separate aromatic
hydrocarbons, specifically of paraxylene or paraxylene
and ethylbenzene from C₈ aromatic isomeric feedstreams
(which may comprise principally ethylbenzene, paraxylene,
orthoxylyene, and metaxylyene), this may be carried out
15 by utilizing zeolites whose internal pore surfaces are
accessible for selective combination of solid and
solute. Examples of suitable zeolites include potassium
substituted zeolite X or Y (synthetic forms of faujasite),
barium substituted zeolite X or Y and rubidium substitu-
20 ted zeolite X. Potassium-substituted zeolite Y is
particularly preferred.

The preparation of such zeolite adsorbent is well known
- for example, potassium-substituted zeolite Y (for
convenience referred to as "potassium-Y" or "K-Y") may
25 be synthesized from Na, K-aluminosilicate gels or
manufactured by a relatively simple ion exchange with a

1 potassium salt carried out on commercially available
sodium-Y-faujasite (Na-Y). Na-Y may in turn be prepared
for example as described in US 3 130 007, US 4 178 352
and US 4 175 059. For the preferred separation of
5 aromatic hydrocarbons the faujasite preferably has a
silica to alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of less than
about 5:1, and preferably about 3.8-4.9:1 (higher
ratios are normally detrimental to the separation of
paraxylene from other C_8 isomers). Potassium-Y-
10 faujasite has been found to be an exceptional adsorbent
for separating the xylene isomers; paraxylene being
selectively adsorbed in the presence of metaxylene,
orthoxylene, and ethylbenzene. The observed order of
sorbability for xylene isomers on potassium-Y-faujasite
15 is paraxylene > ethylbenzene > metaxylene > orthoxylene.

Other adsorbent zeolites may be desirable where different
molecules are to be adsorbed, and as used herein the
term "zeolites" includes not only aluminosilicate
forms, but also low aluminium or substantially aluminium-
20 free silicates with a zeolite structure and analogues
of aluminosilicates in which the tetrahedrally coordina-
ted aluminium in the zeolite structure is replaced by
one or more elements such as gallium, boron or iron.
The preparation of individual zeolites may vary, but in
25 general comprises preparation of a reaction mixture
containing a source of silicon, a source of cations

1 and, unless a substantially pure silica form is required,
a source of modifying element (typically aluminium as
described hereinbefore, but alternatively a source of
an element such as boron, gallium or iron). This
5 reaction mixture is then held under appropriate
crystallization conditions until the desired zeolite is
formed, which may thereafter be modified by subsequent
chemical treatment such as ion exchange. The particular
synthesis techniques to be employed, including the use
10 of additional template molecules, particular cations or
anions, reaction temperatures and pressures are well
documented for each known zeolite. The invention will
be described in terms of zeolite Y but it is believed
to be within the competence of one skilled in the art
15 to adapt the technique to preparing magnetizable forms
of other zeolites, e.g. zeolite A, L, mordenite,
omega or ZSM-5.

In a preferred aspect of the invention there is provided
a process for the preparation of magnetizable adsorbant
20 particles comprising zeolite Y.

As indicated hereinbefore, the preparation of Zeolite
Y is well described in the literature, and it is
believed to be within the competence of one skilled in
the art to prepare a reaction mixture for forming
25 zeolite Y. According to the invention the magnetizable
particles may be introduced into such reaction mixtures
so that zeolite Y is formed therearound.

1 By way of illustration, preferred reaction mixtures
comprise reactants in the following molar ratios
(expressed in terms of oxides):

		<u>Preferred</u>	<u>Highly Preferred</u>
5	$\text{Na}_2\text{O}/\text{SiO}_2$	= 0.4-0.6	0.40-0.48
	$\text{SiO}_2/\text{Al}_2\text{O}_3$	= 8 -20	10-15
	$\text{H}_2\text{O}/\text{Na}_2\text{O}$	= 12 -48	15-20

The reaction mixture is preferably seeded with a slurry
10 comprising 4 to 10 wt%, more preferably 6 to 8 wt.%, of
the reaction mixture and having a composition in the
following molar ratios:

		<u>Preferred</u>
15	$\text{Na}_2\text{O}/\text{SiO}_2$	= 0.8 - 1.3
	$\text{SiO}_2/\text{Al}_2\text{O}_3$	= 3 - 20
	$\text{H}_2\text{O}/\text{Na}_2\text{O}$	= 5 - 45

According to the invention, the substrate to be coated is
introduced into the reaction mixture prior to the
formation of zeolite Y.

20 The substrate may be metal or non-metal selected having
regard to the intended function of the coated substrate.
Thus, the substrate may be, for example, a metal such
as aluminium, iron, steel, stainless steel, nickel or
titanium, a sintered metal material or a refractory or
25 ceramic material such as a glass, magnesia, alumina,

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- 1 silica or other inorganic oxide, silicate or carbide.
The substrate may be in the form of extended bodies
such as bars, balls, chains, mesh, plates, sheets,
tubes or wires, or in the form of discrete particles.
- 5 In a preferred aspect this invention relates to forming
zeolite coatings on magnetizable substrates, and
particularly magnetizable particles, to give a compo-
site product suitable for use as an adsorbent in a
magnetically stabilized bed.
- 10 The preferred magnetizable particles may be formed of a
material which is magnetic in an externally applied
magnetic field or magnetic per se, and are preferably
formed of a ferromagnetic element or compound. These
particles should:
- 15 1) not inhibit zeolite formation;
2) be stable under zeolite preparation conditions;
3) preferably have a high saturation magnetization
to minimise the amount of magnetizable material
in the adsorbent. (This criterion could also be
20 met by chemical and/or physical treatment to
increase the saturation magnetization of the
magnetizable particles - e.g. by chemical
reduction to a more highly magnetizable form);
- 4) preferably have a high Curie temperature so that
25 the adsorbent may be used in high temperature
process;
- 5) preferably have a similar thermal expansion
behaviour to the zeolite.

1 Preferred materials are ferromagnetic metals such as
iron, cobalt and their alloys such as steels, and
ferromagnetic compounds such as magnetite (Fe_3O_4).
The particles preferably have a mean diameter of
5 greater diameter than 20 \AA , more preferably from 100 \AA
to 200 μ , most preferably from 2 to 50 μ .

The magnetizable particles are preferably added in an
amount of from 0.5 to 90 wt% of the combined weight of
reaction mixture plus magnetizable particles, more
10 preferably from 1 to 20 wt% of that combined weight,
most preferably 10 to 20 wt%.

The magnetizable particles are added so that zeolite is
formed thereon, and it has been found advantageous for
the magnetizable particles to be introduced prior to
15 initiating crystallization by heating the reaction
mixture.

On heating the reaction mixture containing the magneti-
zable particles to an appropriate zeolite forming
temperature for an appropriate time zeolite is formed
20 on the magnetizable particles resulting in the forma-
tion of magnetizable zeolite composites. A wide range
of crystallization temperatures and times may be used
but, preferably the reaction mixture is heated to from
60 to 120°C for from 7 to 20 hours.

1 In a preferred embodiment the reaction mixture contain-
ing the magnetizable particles is heated in a rotatable
vessel which is rotated about an inclined axis so that
as the zeolite is formed it forms a layer on the
5 surface of those particles. The rotation is believed
to effect distribution of the particles through the
reaction mixture ensuring that substantially the total
surface of each particle is exposed to the reaction
mixtures so resulting in a more even layer of zeolite
10 formation. The rotational axis of the vessel is
inclined to the vertical so that the particles are kept
in motion and tumble within the reaction mixture. It
is preferred that the particles are alternately lifted
out and fall back into the reaction mixture. It is
15 surprising that simply stirring the reaction mixture
does not have the same beneficial effect in improving
the formation of the zeolite layer on the magnetizable
particles - this is thought to be because stirring
causes considerable agitation of the reaction mixture
20 giving rise to nucleation centres therein.

The axis of rotation is preferably inclined at an angle
of 5° to 90° to the vertical, more preferably at 50°
to 80° and most preferably at 60° to 70°. The vessel
is preferably rotated at a sufficient speed to ensure
25 mixing of the particles within the reaction mixture by
tumbling. Preferably the vessel is rotated at from 5
to 500 rpm, more preferably 10 to 50 rpm.

1 It is a particularly surprising feature of the invention
that the process is capable of forming magnetizable
zeolite particles comprising a magnetizable core having
a substantially complete layer of zeolite formed
5 therearound. The magnetizable core materials are not
zeolitic in structure so that it might be expected that
the zeolite would preferentially form separate non-
magnetizable zeolite particles rather than form a
layer, and it is surprising that the technique of the
10 invention not only brings about formation of a zeolite
coating but that this can form a substantially complete
layer.

Following formation of the coated substrate the product
may be treated to enhance adsorption properties. In
15 particular, a preferred product will comprise in whole
or in the major part Na-Y which may be ion exchanged
with a solution of a potassium salt, preferably potas-
sium nitrate or chloride, to give the corresponding
K-Y product.

20 The invention extends to a method of separating aromatic
hydrocarbons using a magnetically stabilised fluidised
bed of adsorbent particles, in which the particles are
prepared by the process of the invention.

The process preferably involves providing a bed of
magnetizable adsorbent particles which are fluidized by
25 the flow of liquid through the bed; applying a magnetic
field to the bed to stabilize the orientation of the

1 bed; adsorbing components of a liquid feedstream of
hydrocarbons by passing the feedstream through the bed;
and desorbing the adsorbed components with a desorbent.
Efficiency of separation of the hydrocarbon components
5 is increased by the use of adsorbent particles which
pass through a 40 mesh screen, US Standard, while being
able to maintain high liquid velocity (throughput) but
without the high pressure drops which hampered previous
fixed bed processes.

10 Once the hydrocarbon component of the feedstock is
adsorbed onto the particular adsorbent material, it is
removed by the use of a selected desorbent. This
desorbent is a material which is capable of displacing
the sorbate components of the feedstock material. The
15 desorbent selected may be diluted to obtain the desired
strength relative to the hydrocarbon being separated.
If the diluent is not adsorbed, then the combined
desorbent plus diluent stream is most precisely
described as eluent. However, as many nominal diluents
20 may themselves actually serve as extremely weak desor-
bents, for the purposes of the present invention the
combined stream will be referred to as desorbent. For
example, the desorbent used in the separation of xylene
isomers may be a mixture of toluene and carrier, such
25 as C₁₀ to C₁₄ linear paraffins; toluene acts by
competing with the xylene isomers (or other feed

components) for the active sites. Among the suitable desorbents, and particularly useful in the separation of isomeric C₈ aromatic hydrocarbons, are toluene, m-diisopropylbenzene, p-diethylbenzene, mixtures
5 of diethylbenzene isomers, o-dichlorobenzene, and the like. This list, of course, is not all encompassing; other desorbents may be selected provided that they are capable of displacing the sorbent components of the feedstock material.

10 The use of the zeolite composites of the invention in such processes as the adsorbent is advantageous since the composites of the invention provide smaller adsorbent particles than obtained by conventional methods which act as efficient adsorbents and may in a magneti-
15 cally stabilised bed be used without the pressure drop problems normally associated with small particles. Moreover, the composites of the invention by having the zeolite material as a relatively thin layer over magnetizable particles avoid the drawback of conven-
20 tional adsorbents where much of the zeolite is trapped within large agglomerate where its adsorbent properties are not utilised.

The following Examples are now given, though only by way of illustration, to show certain aspects of the
25 invention in more detail.

1 Test Methods: Measurement of Magnetic Yield

To evaluate the products of the process of the invention, test methods were developed to determine the percentage of the adsorbent (zeolite Y) synthesized that was made magnetizable - i.e. that is, the zeolite Y adhering to the magnetizable core particle.

The magnetic yield is defined as:

10 Magnetic yield =
$$\frac{(\text{wt magnetizable fraction}) - (\text{wt metal in sample})}{(\text{wt total sample}) - (\text{wt metal in sample})} \times 100\%$$

To determine this magnetic yield, it was necessary to be able to separate magnetic and non-magnetic fraction of the products. This was carried out as follows.

Procedure:

15 1 gram of carefully crushed sample and 20 ml acetone were added to a 20 ml sample-tube. The tube was closed and shaken, then a composite of three magnets (Tamson-Alnico N 4005) was place on the bottom of the tube which was subjected to a second shaking. The magnetic particles were attracted by the magnet. The liquid and non-magnetic particles were decanted off.

The same procedure was repeated a second time. Only a minor amount of further non-magnetic particles were removed in the second treatment. Acetone which remained in the tube was soaked up with a dry paper tissue and finally the sample-tube was loosely covered with

aluminium foil and dried for 1 hour at 100°C. After cooling for 10 - 15 minutes at room temperature the magnetic residue was weighed. The magnetic yield was then calculated as described above.

5 SEM Assessment

The particles produced by the invention were also investigated using scanning electron microscope (SEM) photography. These enabled individual particles to be seen and a visual assessment made of the percentage of
10 the magnetizable particle covered by zeolite to be estimated.

Example 1: Preparation of Magnetizable Zeolite Y

A mixture was made of 9.61 g alumina trihydrate and 32.56 g sodium hydroxide in 23.75 g water and 49.99 g
15 of 3-4 micron iron spheres were added. The mixture was stirred for 15 seconds. Then 148.37g of Ludox HS-40 (a commercially available silica gel) was added and stirring continued for 1/2 minute. Subsequently, a slurry of amorphous nucleation centres (slurry-compo-
20 sition: $16\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:15\text{SiO}_2:320\text{H}_2\text{O}$) was added and stirring was continued for another 1/2 minute. The resulting gel had the molar composition:
 $6.9\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:16.0\text{SiO}_2:115\text{H}_2\text{O}$.

The entire mixture was placed in a rotatable vessel
25 mounted within an oil bath so that its axis of rotation was at an angle of 60° to the vertical. The vessel was rotated at 25 rpm at 98°C.

1 74.69 of product was obtained (a yield of 10.9 Na-Y)
containing 66.8 wt% Fe and this was analysed by
scanning electron microscopy and found to comprise
magnetizable particles substantially completely coated
5 with zeolite Y. The magnetic yield of the product
was determined as 92%.

Comparative Example 1

To provide a comparison, a similar preparation to
Example 1 was carried out in which the reaction mixture
10 of this zeolite crystallization gel and 30g of 3-4
micron iron particles was heated in a stationary vessel
at 97°C for 16.5 hours, the vessel being simply stirred
at 25 rpm. 55.15g of product was obtained containing
54.4 wt% Fe. This had a magnetic yield of 42% and SEM
15 showed only 25 % of the iron particles to be effectively
covered with zeolite.

Comparative Example 2

The procedure of Example 1 was again repeated. The
zeolite Y forming reaction mixture had the composition:
20 $6.9\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:16\text{SiO}_2:112\text{H}_2\text{O}$, and the entire
mixture of this zeolite crystallization gel and 30g of
3-4 micron iron particles was heated in a static
crystallization for 16 hours at 98°C. 54.06g of
product was obtained containing 55.5 wt% iron particles.
25 This had a magnetic yield of 43% and SEM showed again
only 25% of the iron particles to be covered with
zeolite.

1 The Comparative Examples show that the process of the
invention enables a more complete covering of magnetiz-
able particles by a zeolite layer to be achieved.

Examples 2-3 and Comparative Examples 3-4

5 In Examples 2 and 3 the general procedure outlined in
Example 1 was repeated using different magnetizable
particles. In Comparative Examples 3 and 4 the stirred
synthesis described in Comparative Example 1 was
repeated using the magnetizable particles of Examples 2
10 and 3. The results of all the Examples are given in
Table 1 below.

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Example

Table 1

Example	Zeolite Reaction mixture - molar composition	Magnetizable Particles amount (g)/ size (micron)/type	Reaction Vessel mixing/speed (rpm)	Product magnetic yield (%)	Surface of particles covered by zeolite (%)
Example 1	6.9Na ₂ O:Al ₂ O ₃ :16.0SiO ₂ :115H ₂ O	49.9/3-4/iron	Rotated 25 rpm at 60° to vertical	92	100%
Comp. Ex. 1	6.9Na ₂ O:Al ₂ O ₃ :16.0SiO ₂ :120H ₂ O	30.0/3-4/iron	Stirred 25 rpm	42	25%
Comp. Ex. 2	6.9Na ₂ O:Al ₂ O ₃ :16.0SiO ₂ :112H ₂ O	30.0/3-4/iron	Static 0 rpm	43	25%
Example 2	6.9Na ₂ O:Al ₂ O ₃ :16.0SiO ₂ :115H ₂ O	30.0/10-50/stainless steel	Rotated 25 rpm at 60° to vertical	12	90%
Comp. Ex. 3	6.9Na ₂ O:Al ₂ O ₃ :16.0SiO ₂ :115H ₂ O	30.0/10-50/stainless steel	Stirred 25 rpm	13	25%
Example 3		50.8/<40/magnetite	Rotated 25 rpm at 60° to vertical	55	100
Comp. Ex. 4		40.0/<40/magnetite	Stirred 25 rpm	58	100

CLAIMS

1. A process for the preparation of a zeolite layer upon a substrate which does not have the same crystalline structure as the zeolite, in which process the substrate is contacted with a reaction mixture for forming a zeolite and the reaction mixture is heated to bring about zeolite formation, in which the substrate is tumbled within the reaction mixture during heating so as to cause zeolite formation preferentially as a layer on the surface of the substrate.
2. A process as claimed in claim 1, in which the substrate is introduced into a rotatable vessel containing a reaction mixture for forming the zeolite, the reaction mixture is heated to form zeolite, and during the heating the vessel is rotated about an axis inclined to the vertical so that zeolite is formed as a layer on the surface of the substrate.
3. A process for the preparation of magnetizable adsorbant particles for use in a magnetically stabilized bed, in which process magnetizable particles are introduced into a rotatable vessel containing a reaction mixture for forming a zeolite, the reaction mixture is heated to bring about zeolite formation, and during the heating the vessel is rotated about an inclined axis so that the zeolite is formed as a layer on the surface of the magnetizable particles.

4. A process for the preparation of magnetizable particles comprising zeolite Y for use in a magnetically stabilized bed, in which process magnetizable particles are introduced into a rotatable vessel containing a reaction mixture for forming zeolite Y, the reaction mixture is heated to form zeolite Y, and during the heating the vessel is rotated about an inclined axis so that zeolite Y is formed as a layer on the surface of the magnetizable particles.

5. A process as claimed in claim 4, in which the reaction mixture is an aqueous composition comprising sodium, silica, alumina and water in the following ratios, expressed in terms of mole ratios of oxides:

$\text{Na}_2\text{O}/\text{SiO}_2$	=	0.38-0.60
$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	8-20
$\text{H}_2\text{O}/\text{Na}_2\text{O}$	=	12-48

6. A process as claimed in claim 5, in which the reaction mixture comprises reactants in the following molar ratios, expressed in terms of oxides:

$\text{Na}_2\text{O}/\text{SiO}_2$	=	0.40 - 0.48
$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	10 - 15
$\text{H}_2\text{O}/\text{Na}_2\text{O}$	=	15-20

7. A process as claimed in claim 4 or 5, in which the reaction mixture is seeded with a slurry comprising 4 to 10 wt% of the reaction mixture and having a composition in the following molar ratios:

Na ₂ O/SiO ₂	=	0.8 - 13
SiO ₂ /Al ₂ O ₃	=	3 - 20
H ₂ O/Na ₂ O	=	5 - 45

8. A process as claimed in any of claims 3 to 7, in which the magnetizable particles are particles of iron, cobalt, steel or magnetite.
9. A process as claimed in any of claims 3 to 8, in which the particles have a mean diameter of from 2 to 50 microns.
10. A process as claimed in any of claims 3 to 9, in which the reaction mixture contains from 1 to 20 wt% of magnetizable particles.
11. A process as claimed in any of claims 4 to 10, in which the formed magnetizable zeolite particles comprise the sodium form of zeolite Y which is thereafter ion exchanged with a solution of a potassium salt to form the corresponding potassium form of zeolite Y.
12. A process as claimed in any of claims 2 to 11, in which the vessel is rotated about an axis inclined at an angle of from 30° to 85° to the vertical.
13. A process as claimed in claim 12, in which the axis of rotation is at an angle of 50° to 80° to the vertical.

14. A process as claimed in any of claims 2 to 13, in which the speed of rotation of the vessel is from 5 to 500 rpm.
15. A process as claimed in any of claims 3 to 14, in which the zeolite is formed as a substantially complete layer around the magnetizable particles.
16. A magnetizable zeolite particle comprising a magnetizable core having a substantially complete layer of zeolite formed therearound.
17. A method of separating aromatic hydrocarbon using a magnetically stabilised fluidised bed of adsorbent particles prepared by a process as claimed in any of claims 3 to 15.

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EP 84308837.8

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	GB - A - 2 059 795 (EXXON) * Pages 6,7; claims * --	1,8-11	B 01 J 20/18 B 01 J 2/12 // C 07 C 7/13
D,Y	EP - A1 - 0 055 044 (EXXON) * Claims; examples 1-6 * --	1,8-11	
Y	DE - A1 -2 805 546 (KALI) * Claims * --	1	
A	GB - A - 2 002 254 (EXXON) * Pages 2,3; claims * --	1,8,17	
A	EP - A1 - 0 083 202 (EXXON) * Page 7, line 30 - page 9, line 29; claims * --	1,8,11,17	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	US - A - 4 399 047 (SEIVER et al.) * Column 7, line 26 - column 11, line 68; claims * ----	1,2,8,11	B 01 J C 07 C 7/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 02-04-1985	Examiner TENGLER
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